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<b>(21) International Application Number:</b> PCT/US96/14847 <b>(22) International Filing Date:</b> 13 September 1996 (13.09.96)  <b>(30) Priority Data:</b> 08/528,070 14 September 1995 (14.09.95) US  <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).  <b>(72) Inventors:</b> CHEN, Michael, Chia-Chao; 1504 Chimney Rock, Houston, TX 77056 (US). MEHTA, Aspy, Keki; 5611 Forest Timbers, Humble, TX 77346 (US).  <b>(74) Agents:</b> SCHMIDT, C., Paige et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US).		<b>(81) Designated States:</b> BR, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROPYLENE POLYMER BLENDS AND FILMS AND ARTICLES MADE THEREFROM		
<b>(57) Abstract</b>  Propylene polymer blend compositions are provided wherein the blend comprises propylene copolymer having a broad molecular weight distribution and metallocene produced propylene copolymer. The blend composition has a wide variety of uses. Films made from such blends exhibit low extractables, enhanced heat seal performance, clarity, gloss, and toughness when compared to films produced from conventional copolymers. The balance of film properties achieved is unique compared to films made from the individual components of the blend.		

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**PROPYLENE POLYMER BLENDS AND FILMS AND ARTICLES MADE  
THEREFROM**

**FIELD OF THE INVENTION**

5           This invention relates generally to polymer blend compositions and to films, fabrics and articles made from such blends. The blend comprises propylene copolymer having a broad molecular weight distribution and metallocene produced propylene copolymer. The blend composition has a  
10 wide variety of uses. Films made from such blends exhibit low extractables, enhanced heat seal performance, clarity, gloss, and toughness when compared to films produced from conventional copolymers. Films made from the blends of this invention have a unique balance of properties as compared to  
15 films made from the individual components used to make the blend.

**BACKGROUND**

20           Propylene random copolymers are used in many applications. One major area of use is in film packaging applications where the copolymer forms the heat sealing layer in the overall film construction. The random copolymers used commercially today include  
25 propylene/ethylene copolymers and propylene/ethylene/butene terpolymers.

          WO 92/14784 and United States Patent No. 5,358,792 disclose films made from a blend of a metallocene catalyzed  
30 ethylene based copolymer and a propylene based polymer. EP 0 499 216 A1 discloses molded articles made from a composition comprising polypropylene having a substantially syndiotactic structure and a copolymer of ethylene and propylene.

35

          We have found that film properties can be significantly enhanced by making the film from a blend of metallocene

produced propylene copolymer and propylene copolymer having a broad molecular weight distribution.

### Summary

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The present invention relates generally to a propylene polymer blend composition comprising, (a) from about 25 to about 75 weight percent based on the total weight of the polymer blend of a first propylene polymer that is

10 substantially isotactic and is comprised of at least about 80 weight percent propylene units based on the total weight of the polymer and has a molecular weight distribution of at least about 2.5; and (b) from about 25 to about 75 weight

15 percent based on the total weight of the polymer blend of a second propylene polymer that is substantially isotactic and is comprised of at least about 80 weight percent propylene units based on the total weight of the polymer and from about 0.2 to about 10 weight percent based on the total

20 weight of the polymer of a second alpha olefin comonomer having 5 or more carbon atoms, wherein the second polymer is made using a metallocene catalyst. The present invention is also directed toward films, fabrics and articles made using the above described blend.

### 25 Detailed Description

The polymer blend of the invention comprises first and second propylene polymers, preferably at least one of which is substantially isotactic, more preferably, both polymers

30 are substantially isotactic, most preferably, both polymers are isotactic.

"Substantially isotactic" is defined herein to mean that the percentage of isotactic pentads (mmmm) in

35 homopolypropylene (made under the same conditions and using the same catalyst system as the polymer in question taking into account those differences required for

homopolymerization versus copolymerization) is greater than about 80%. "Isotactic" is defined herein to mean that the percentage of isotactic pentads (mmmm) in homopolypropylene (made using the same catalyst system and made under the same conditions as the polymer in question taking into account those differences required for homopolymerization versus copolymerization) is greater than about 90%. As used herein, copolymer includes polymers comprising 2 or more monomers.

The first polymer has a broad molecular weight distribution and comprises from about 25 to about 75 weight percent of the blend, preferably from about 30 to about 70 weight percent, more preferably from about 40 to about 60 weight percent of the blend, and most preferably about 50 weight percent of the blend based on the total weight of the blend.

The second polymer is metallocene catalyzed and likewise comprises about 25 to about 75 weight percent of the blend, preferably about 30 to about 70, more preferably about 40 to about 60 weight percent of the blend, most preferably about 50 weight percent of the blend based on the total weight of the blend.

Preferably the first polymer of the blend is produced using a Zeigler-Natta type catalyst system. The molecular weight distribution ( $M_w/M_n$  - as determined by gel permeation chromatography) of the first polymer is broad, i.e., at least about 2.5, preferably from about 2.5 to about 10, more preferably from about 3.5 to about 7.0.

The first polymer preferably has a broad composition and tacticity distribution. It is well known in the art that propylene copolymers prepared via conventional Zeigler-Natta catalysts, which are multi-sited, have a non-homogeneous distribution of comonomers among molecules and

of tacticity arrangement among molecules. This broader distribution shows up most directly in the volatile and extractable content of the resin as well as in its physical properties. This has been shown by McAlpin and Stahl,  
5 Metcon 1994 Proceedings (May 25, 1994).

Preferably the first polymer is a substantially isotactic, random copolymer of propylene units and up to about 10 weight percent of comonomer based on the total  
10 weight of the copolymer, preferably the copolymer contains from about 2 to about 7 weight percent comonomer, most preferably from about 4 to about 6 weight percent comonomer. The comonomer may be any comonomer or any combination of comonomers, however, preferably the comonomer is ethylene  
15 and/or butene-1.

The first propylene polymer may be prepared by any method which yields a propylene polymer having the characteristics described above. Preferably the first  
20 propylene polymer is prepared using a Zeigler-Natta type catalyst system. It is well known that such catalysts yield polymers and copolymers having a broad molecular weight distribution. Typically such systems comprise a transition metal halide, such as titanium or vanadium halide, and an  
25 organometallic compound of a metal of Group 1, 2, or 3, typically trialkylaluminum compounds, which serve as the transition metal halide activator. Some Zeigler-Natta catalyst systems incorporate an internal electron donor which is complexed to the alkyl aluminum or the transition  
30 metal. Chromium catalysts such as those described in U.S. Patent 4,460,755 (fully incorporated herein by reference) are also considered herein to be Zeigler-Natta catalysts. The following may be referred to for details regarding Zeigler-Natta catalysts: U.S. Patent Nos. 3,687,920;  
35 4,086,408; 4,376,191; 5,019,633; 4,482,687; 4,101,455, 4,560,671; 4,719,193; 4,755,495; and 5,070,055 each of which is fully incorporated herein by reference.

The first propylene polymer preferably has a weight average molecular weight that is greater than about 150,000, preferably in the range of from about 150,000 to about 320,000, more preferably in the range of from about 190,000 to about 300,000. The melt flow rate of the first propylene polymer is generally in that range useful for films; in the range of from about 1 dg/min. to about 20 dg/min., preferably in the range of from about 2 dg/min. to about 10 dg/min., more preferably in the range of from about 3 dg/min. to about 7 dg/min. as measured by ASTM-D1238 condition L.

The second propylene polymer of the blend is produced by one or more metallocene catalyst systems. Preferably, the second propylene polymer has a molecular weight distribution ( $M_w/M_n$  - as determined by gel permeation chromatography) that is less than about 3.0, preferably from about 2.5 to about .5, more preferably from about 2.5 to about 1.5. The second propylene polymer is a copolymer of propylene and at least about .2 weight percent comonomer, preferably from about .2 to about 20 weight percent comonomer, more preferably from about 1. to about 15 weight percent comonomer, even more preferably from about 1.5 to about 10 weight percent comonomer, and most preferably from about 2.0 to about 6 weight percent comonomer based on the total weight of the copolymer.

The comonomer preferably has 5 or more carbon atoms, more preferably the comonomer has from 5 to 20 carbon atoms, even more preferably the comonomer has from 5 to 10 carbon atoms, and most preferably the comonomer is selected from the group consisting of pentene-1, hexene-1 and octene-1.

The second propylene polymer preferably has a weight average molecular weight that is greater than about 150,000, preferably in the range of from about 150,000 to about

320,000, more preferably in the range of from about 190,000 to about 300,000. The melt flow rate of the second propylene polymer is in that range useful for films, preferably from about 1 dg/min. to about 20 dg/min., more preferably in the range of from about 2 dg/min. to about 10 dg/min. as measured by ASTM-1238 condition L.

The second polymer preferably has a narrow composition and tacticity distribution. It is well known in the art that metallocene-based catalysts, which are single-sited, make propylene copolymers having a homogeneous distribution of comonomer among molecules and a uniform tacticity arrangement among molecules. The effect of this narrow composition and tacticity distribution shows up vividly in the low extractable content of these resins. As will be described in more detail later, Table 1 quantifies the extractables level of some examples of metallocene-derived propylene copolymer at 0.7 weight percent versus a conventional Zeigler-Natta-derived propylene copolymer of comparable crystallinity at 3.3 weight percent.

The second propylene polymer is preferably a substantially isotactic random copolymer and is prepared using a metallocene catalyst system. Any metallocene may be used in the present invention. Metallocenes are generally represented by the formula



wherein Cp is a cyclopentadienyl ring or derivative thereof, M is a Group 4, 5, or 6 transition metal, R is a hydrocarbyl group or hydrocarboxy group having from 1 to 20 carbon atoms, X is a halogen, and  $m=1-3$ ,  $n=0-3$ ,  $q=0-3$ , and the sum of  $m+n+q$  is equal to the oxidation state of the transition metal. The metallocene may be bridged or unbridged, and include heteroatoms in the structure. Examples of metallocenes are discussed in for example, U.S. Patent Nos. 4,530,914; 4,871,705; 4,937,299; 5,124,418; 5,017,714; 5,120,867; 5,278,119; 5,304,614; 5,324,800; 5,347,025;

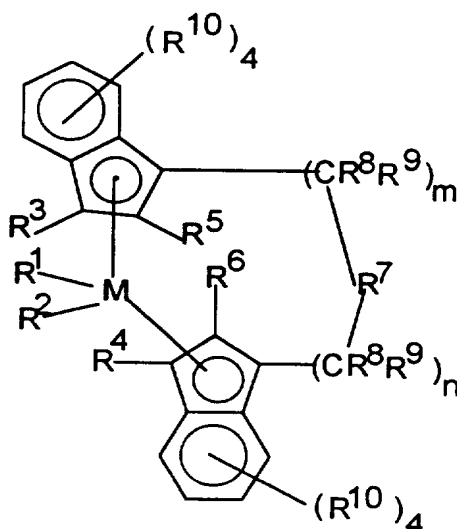


5,350,723; 5,391,790; and 5,391,789; EP-A- 0 591 756; EP-A-0 520 732; EP-A-0 420 436; WO 91/04257; WO 93/08221; WO 93/08199; and WO 94/01471 each incorporated fully herein by reference.

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Particularly preferred metallocene components comprise a Group 4, 5, or 6 transition metal, biscyclopentadienyl derivative, preferably bis-indenyl metallocene components having the following general structure:

10



wherein M is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium;

15

R<sup>1</sup> and R<sup>2</sup> are identical or different, are one of a hydrogen atom, a C<sub>1</sub>-C<sub>10</sub> alkyl group, preferably a C<sub>1</sub>-C<sub>3</sub> alkyl group, a C<sub>1</sub>-C<sub>10</sub> alkoxy group, preferably a C<sub>1</sub>-C<sub>3</sub> alkoxy group, a C<sub>6</sub>-C<sub>10</sub> aryl group, preferably a C<sub>6</sub>-C<sub>8</sub> aryl group, a C<sub>6</sub>-C<sub>10</sub> aryloxy group, preferably a C<sub>6</sub>-C<sub>8</sub> aryloxy group, a C<sub>2</sub>-C<sub>10</sub> alkenyl group, preferably a C<sub>2</sub>-C<sub>4</sub> alkenyl group, a C<sub>7</sub>-C<sub>40</sub> arylalkyl group, preferably a C<sub>7</sub>-C<sub>10</sub> arylalkyl group, a C<sub>7</sub>-C<sub>40</sub> alkylaryl group, preferably a C<sub>7</sub>-C<sub>12</sub> alkylaryl group, a C<sub>8</sub>-C<sub>40</sub> arylalkenyl group, preferably

20

25

a C<sub>8</sub>-C<sub>12</sub> arylalkenyl group, or a halogen atom, preferably chlorine;

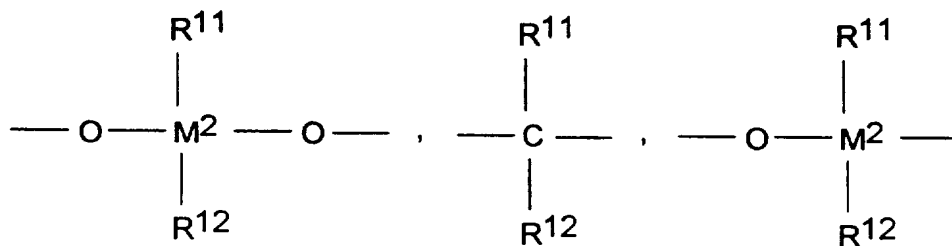
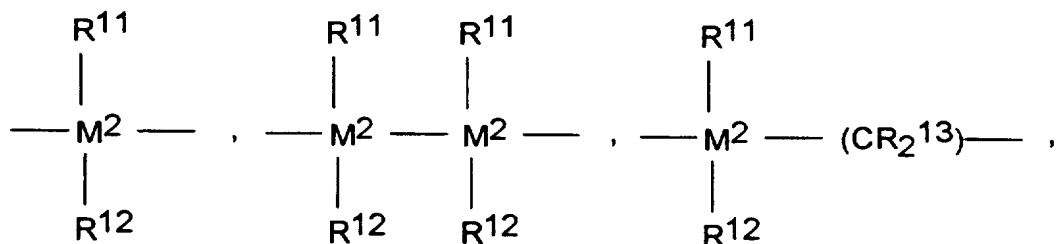
R<sup>3</sup> and R<sup>4</sup> are hydrogen atoms;

5

R<sup>5</sup> and R<sup>6</sup> are identical or different, preferably identical, are one of a halogen atom, preferably a fluorine, chlorine or bromine atom, a C<sub>1</sub>-C<sub>10</sub> alkyl group, preferably a C<sub>1</sub>-C<sub>4</sub> alkyl group, which may be halogenated, a C<sub>6</sub>-C<sub>10</sub> aryl group, which may be halogenated, preferably a C<sub>6</sub>-C<sub>8</sub> aryl group, a C<sub>2</sub>-C<sub>10</sub> alkenyl group, preferably a C<sub>2</sub>-C<sub>4</sub> alkenyl group, a C<sub>7</sub>-C<sub>40</sub> -arylalkyl group, preferably a C<sub>7</sub>-C<sub>10</sub> arylalkyl group, a C<sub>7</sub>-C<sub>40</sub> alkylaryl group, preferably a C<sub>7</sub>-C<sub>12</sub> alkylaryl group, a C<sub>8</sub>-C<sub>40</sub> arylalkenyl group, preferably a C<sub>8</sub>-C<sub>12</sub> arylalkenyl group, a -NR<sub>2</sub><sup>15</sup>, -SR<sup>15</sup>, -OR<sup>15</sup>, -OSiR<sub>3</sub><sup>15</sup> or -PR<sub>2</sub><sup>15</sup> radical, wherein R<sup>15</sup> is one of a halogen atom, preferably a chlorine atom, a C<sub>1</sub>-C<sub>10</sub> alkyl group, preferably a C<sub>1</sub>-C<sub>3</sub> alkyl group, or a C<sub>6</sub>-C<sub>10</sub> aryl group, preferably a C<sub>6</sub>-C<sub>9</sub> aryl group;

20

R<sup>7</sup> is



=BR<sup>11</sup>, =AlR<sup>11</sup>, -Ge-, -Sn-, -O-, -S-, =SO, =SO<sub>2</sub>, =NR<sup>11</sup>, =CO, PR<sup>11</sup>, or =P(O)R<sup>11</sup>;

wherein:

R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group, preferably a C<sub>1</sub>-C<sub>10</sub> alkyl group, a C<sub>1</sub>-C<sub>20</sub> fluoroalkyl group, preferably a C<sub>1</sub>-C<sub>10</sub> fluoroalkyl group, a C<sub>6</sub>-C<sub>30</sub> aryl group, preferably a C<sub>6</sub>-C<sub>20</sub> aryl group, a C<sub>6</sub>-C<sub>30</sub> fluoroaryl group, preferably a C<sub>6</sub>-C<sub>20</sub> fluoroaryl group, a C<sub>1</sub>-C<sub>20</sub> alkoxy group, preferably a C<sub>1</sub>-C<sub>10</sub> alkoxy group, a C<sub>2</sub>-C<sub>20</sub> alkenyl group, preferably a C<sub>2</sub>-C<sub>10</sub> alkenyl group, a C<sub>7</sub>-C<sub>40</sub> arylalkyl group, preferably a C<sub>7</sub>-C<sub>20</sub> arylalkyl group, a C<sub>8</sub>-C<sub>40</sub> arylalkenyl group, preferably a C<sub>8</sub>-C<sub>22</sub> arylalkenyl group, a C<sub>7</sub>-C<sub>40</sub> alkylaryl group, preferably a C<sub>7</sub>-C<sub>20</sub> alkylaryl group or R<sup>11</sup> and R<sup>12</sup>, or R<sup>11</sup> and R<sup>13</sup>, together with the atoms binding them, can form ring systems;

M<sup>2</sup> is silicon, germanium or tin, preferably silicon or germanium, most preferably silicon;

R<sup>8</sup> and R<sup>9</sup> are identical or different and have the meanings stated for R<sup>11</sup>;

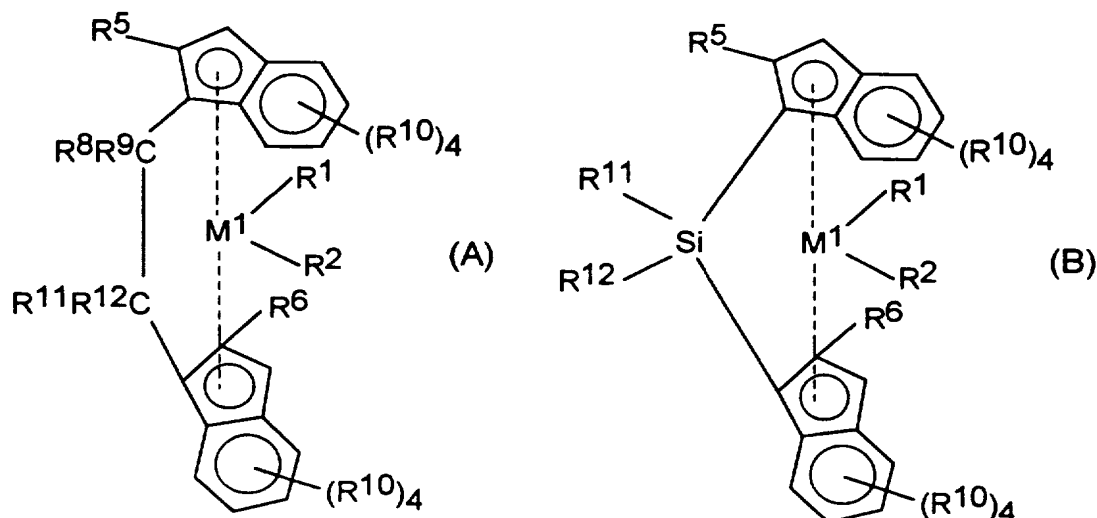
m and n are identical or different and are zero, 1 or 2, preferably zero or 1, m plus n being zero, 1 or 2, preferably zero or 1; and

the radicals R<sup>10</sup> are identical or different and have the meanings stated for R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup>. Two adjacent R<sup>10</sup> radicals can be joined together to form a ring system, preferably a ring system containing from about 4-6 carbon atoms.

Alkyl refers to straight or branched chain substituents. Halogen (halogenated) is fluorine, chlorine, bromine or iodine atoms, preferably fluorine or chlorine.

Particularly preferred metallocenes are compounds of the structures:

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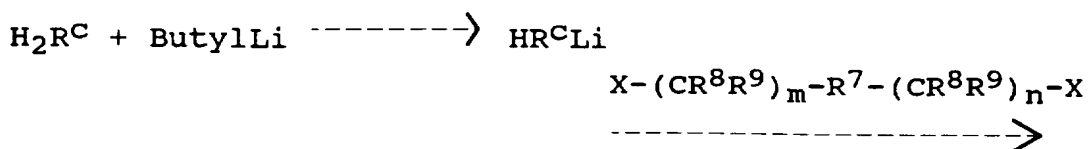


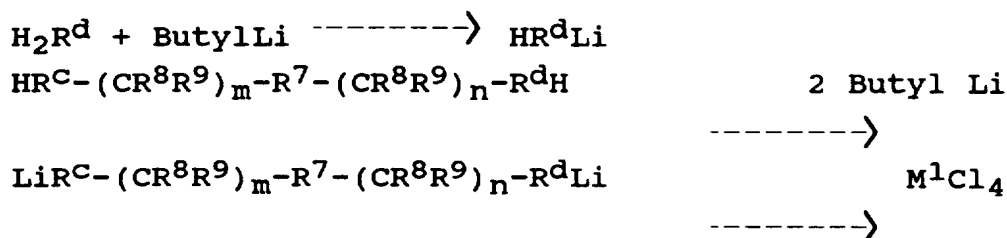
wherein:

M<sup>1</sup> is Zr or Hf, R<sup>1</sup> and R<sup>2</sup> are methyl or chlorine, and R<sup>5</sup>, R<sup>6</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup> and R<sup>12</sup> have the above-mentioned meanings.

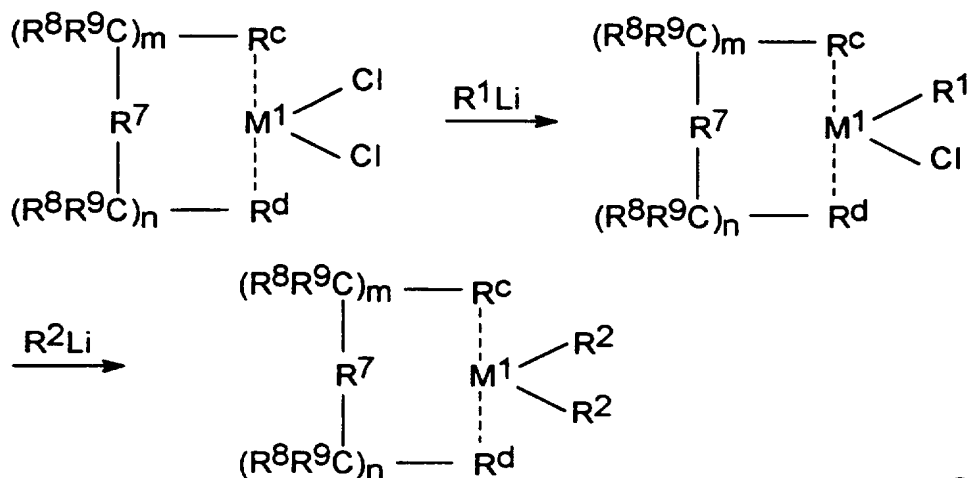
The chiral metallocenes may be used as a racemate for the preparation of highly isotactic polypropylene copolymers. It is also possible to use the pure R or S form. An optically active polymer can be prepared with these pure stereoisomeric forms. Preferably the meso form of the metallocene is removed to ensure the center (i.e., the metal atom) provides stereoregular polymerization. Separation of the stereoisomers can be accomplished by known literature techniques. For special products it is also possible to use rac/meso mixtures.

Generally, the metallocenes are prepared by a multi-step process involving repeated deprotonations/metallations of the aromatic ligands and introduction of the bridge and the central atom by their halogen derivatives. The following reaction scheme illustrates this generic approach:

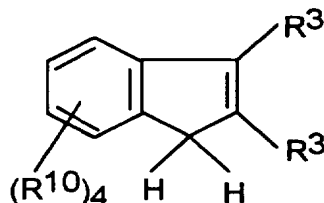




5



X = Cl, Br, I or O-tosyl;

$$\begin{array}{l}
 \text{H}_2\text{R}^c, \\
 \text{H}_2\text{R}^d =
 \end{array}$$


Additional methods for preparing metallocenes are fully described in the Journal of Organometallic Chem., volume 288, (1958), pages 63-67, and in EP-A- 320762, for preparation of the metallocenes described, both of which are herein fully incorporated by reference.

Illustrative but non-limiting examples of metallocenes include:

15 Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl)ZrCl<sub>2</sub>

Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl)ZrCl<sub>2</sub>;

Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)ZrCl<sub>2</sub>;

Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl<sub>2</sub>;

20 Dimethylsilandiylbis (2-ethyl-4-naphthyl-1-indenyl)ZrCl<sub>2</sub>,

Phenyl(Methyl)silandiylbis(2-methyl-4-phenyl-1-indenyl)ZrCl<sub>2</sub>,

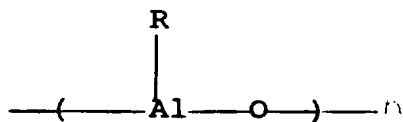
- Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl<sub>2</sub>,  
5 Dimethylsilandiylbis(2-methyl-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
10 1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl<sub>2</sub>,  
15 Dimethylsilandiylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-ethyl-4-methyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2,4-dimethyl-1-indenyl)ZrCl<sub>2</sub>,  
20 Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl- $\alpha$ -acenaphth-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4,5-(methylbenzo)-1-indenyl)ZrCl<sub>2</sub>,  
25 Phenyl(Methyl)silandiylbis(2-methyl-4,5-(tetramethylbenzo)-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl- $\alpha$ -acenaphth-1-indenyl)ZrCl<sub>2</sub>,  
30 1,2-Ethandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Butandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Ethandiylbis(2,4,7-trimethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
35 1,2-Ethandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
Diphenylsilandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,

1,2-Butandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
 Dimethylsilandiylbis(2-ethyl-1-indenyl)ZrCl<sub>2</sub>,  
 Dimethylsilandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl<sub>2</sub>,  
 Phenyl(Methyl)silandiylbis(2-methyl-5-isobutyl-1-  
 5 indenyl)ZrCl<sub>2</sub>,  
 Dimethylsilandiylbis(2-methyl-5-t-butyl-1-indenyl)ZrCl<sub>2</sub>,  
 Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl)ZrCl<sub>2</sub>, and  
 the like.

10        These preferred metallocene catalyst components are  
 described in detail in U.S. Patent Nos. 5,149,819,  
 5,243,001, 5,239,022, 5,296,434 and 5,276,208 all of which  
 are herein fully incorporated by reference.

15        The metallocene may be activated with an ionic  
 activator and/or an alkylalumoxane. Alkylalumoxanes may  
 exist in the form of linear or cyclic polymers. Generally,  
 the alkylalumoxanes preferred for use in olefin  
 polymerization contain about 5 to 40 of the repeating units:

20



25        where R is a C<sub>1</sub>-C<sub>8</sub> alkyl including mixed alkyls.  
 Particularly preferred are the compounds where R is methyl.  
 There are a variety of methods for preparing alumoxane, non-  
 limiting examples of which are described in U.S. Patent No.  
 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419,  
 30 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815,  
 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and  
 EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and WO  
 94/10180, each fully incorporated herein by reference.

35        Some methylalumoxane (MAO) solutions tend to become  
 cloudy and gelatinous over time. It may be advantageous to  
 clarify such solutions prior to use. A number of methods

are used to create gel-free MAO solutions or to remove gels from the solutions. Gelled solutions are often simply shaken or decanted. U.S. Patent No. 5,157,137 discloses a process for forming clear, gel-free solutions of  
5 alkylalumoxane by treating a solution of alkylalumoxane with an anhydrous salt and/or hydride of an alkali or alkaline earth metal.

The metallocene and/or activator may be supported. For  
10 purposes of this patent specification the term "carrier" and "support" are interchangeable and may be any support material, preferably a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides and resinous support materials such as polyolefin or polymeric  
15 compounds or any other organic material that is porous and has an average particle size greater than 10  $\mu\text{m}$ .

The support materials are inorganic oxide materials, which include those from the Periodic Table of Elements of  
20 Groups 2, 3, 4, 5, 13 or 14 metal oxides. Preferably, the catalyst support materials include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania,  
25 zirconia, and the like.

Supported metallocene catalyst systems may be made in a variety of different ways. A general support technique is described in U.S. Patent No. 5,240,894 (fully incorporated  
30 herein by reference). This method involves contacting, in a suitable solvent or other liquid, a metallocene catalyst component as described above with alumoxane or methylalumoxane (MAO) as described above to form a reaction product in solution. The mole ratio of the aluminum of the  
35 alumoxane component to the transition metal of the metallocene component is preferably in the range of ratios



between about 12:1 to about 800:1, preferably 20:1 to less than 500:1, and most preferably 50:1 to less than 400:1.

Ionizing activators, neutral or ionic, may also be used including compounds such as tri (n-butyl) ammonium tetrakis(pentafluorophenyl) boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing compound. Combinations of activators are also contemplated by the invention, for example, alumoxane and ionizing activators in combinations, see for example, WO 94/07928.

Descriptions of ionic catalysts for coordination polymerization comprised of metallocene cations activated by non-coordinating anions appear in the early work in EP-A-0 277 003, EP-A-0 277 004 and US patent 5,198,401 and WO-A-92/00333 (incorporated herein by reference). These teach a preferred method of preparation wherein metallocenes (bisCp and monoCp) are protonated by an anion precursor such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced by the non-coordinating anion.

The term "noncoordinating anion" means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the metallocene cation in the sense of

balancing its ionic charge in a +1 state, yet retain sufficient lability to permit displacement by an ethylenically or acetylenically unsaturated monomer during polymerization.

5

The use of ionizing ionic compounds not containing an active proton but capable of producing both the active metallocene cation and an noncoordinating anion is also known. See, EP-A-0 426 637 and EP-A- 0 573 403 (incorporated  
10 herein by reference). An additional method of making the ionic catalyst systems uses ionizing anion pre-cursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the metallocene compounds, for example the use of tris(pentafluorophenyl) boron. See  
15 EP-A-0 520 732 (incorporated herein by reference). Ionic catalysts for addition polymerization can also be prepared by oxidation of the metal centers of transition metal compounds by anion pre-cursors containing metallic oxidizing groups along with the anion groups, see EP-A-0 495 375  
20 (incorporated herein by reference).

Where the metal ligands include halogen moieties (for example, bis-cyclopentadienyl zirconium dichloride) which are not capable of ionizing abstraction under standard  
25 conditions, they can be converted via known alkylation reactions with organometallic compounds such as lithium or aluminum hydrides or alkyls, alkylalumoxanes, Grignard reagents, etc. See EP-A-0 500 944 and EP-A1-0 570 982 (incorporated herein by reference) for *in situ* processes  
30 describing the reaction of alkyl aluminum compounds with dihalo-substituted metallocene compounds prior to or with the addition of activating anionic compounds.

Methods of supporting ionic catalysts comprising  
35 metallocene cations and noncoordinating anions are described in WO91/09882, WO 94/03506 and in co-pending U.S. Ser. No. 08/285,380, filed August 3 1994 (incorporated herein by

reference). The methods generally comprise either physical adsorption on traditional polymeric or inorganic supports that have been largely dehydrated and dehydroxylated, or using neutral anion precursors that are sufficiently strong Lewis acids to activate retained hydroxy groups in silica containing inorganic oxide supports such that the Lewis acid becomes covalently bound and the hydrogen of the hydroxy group is available to protonate the metallocene compounds.

Any method may be used to produce the polymers of the blend. For example, a gas, slurry or solution phase process may be used. The second propylene polymer is preferably prepared using a gas phase or slurry phase process, most preferably a bulk liquid propylene polymerization process is used.

Any method may be used to combine the first and second propylene polymers. For example a kneader, extruder or mixer such as a Banbury or Farrell mixer that achieves melt homogenization may be used.

The blend of this invention is particularly well suited for use in film applications such as oriented and non-oriented films, cast or blown extruded, mono and multi layer films (including coextruded films and laminated films), heat seal films, composite films and the like.

The films of this invention have a number of improved properties as compared to known films, including but not limited to, better heat seal performance, seal strength, hot tack performance, lower haze, and improved dart impact toughness, and tear toughness all while retaining commercially valuable processing characteristics. Cast monolayer films in particular exhibit exceptional dart impact toughness, and tear toughness and exhibit a balance of film properties that is uniquely different from those of films made from the individual components of the blend.

Given these remarkably improved film properties it is anticipated that other articles made from the blends described herein would also exhibit improved properties while maintaining commercially valuable processability.

5 Specific examples of such other articles include fibers, fabrics, molded articles, cast articles and the like.

Any additive may be incorporated into the blend including but not limited to stabilizers, neutralizers, slip  
10 agents, antiblock agents, nucleating agents, colorants, dyes, flame retardants, pigments, fillers, reinforcements, and the like. Effective amounts are selected based on the application desired, characteristic to be modified, and film fabrication mode, all as known in the art.

15

#### Examples

Films prepared from commercially available, Zeigler-Natta produced, propylene/ethylene random copolymer and  
20 metallocene produced propylene/hexene-1 random copolymer were compared with a 50/50 melt compounded blend of the two. Monolayer films were cast using a Killion laboratory film casting line. The films were then tested for various properties.

25

The Zeigler-Natta produced copolymer, "PD9282 E2", used in these examples is commercially available from Exxon Chemical Company, Houston, Texas, U.S.A.. The properties of PD9282 E2 are detailed in Table 1.

30

The metallocene produced copolymer, "MCN", was prepared in a single, continuous, stirred tank reactor, bulk liquid-phase polymerization process using rac-  
dimethylsilanediylbis(2-methyl-4,5-benzo-indenyl)zirconium  
35 dichloride activated with methylalumoxane. A method for preparing rac-dimethylsilanediylbis(2-methyl-4,5-benzo-indenyl)zirconium dichloride may be found in EP A 549 900

and CN 2,084,017 (each fully incorporated herein by reference).

The supported catalyst system was prepared in the following manner. Methylalumoxane (obtained from Albemarle Corp., Baton Rouge, LA, USA) was added to an eight-liter vessel equipped with a cooling jacket and an efficient overhead stirrer. With stirring, a suspension of 5.0 g of rac-dimethylsilanediylbis(2-methyl-4,5-benzo-indenyl)zirconium dichloride in toluene (700ml) was added under N<sub>2</sub> through a double-ended needle. After stirring for 10 min., dehydrated silica (200 g Davison 948, dried at 800°C) was added to the solution over 20 minutes. The slurry was stirred for 10 minutes and then, while vacuum was applied from the top of the vessel, a slight flow of N<sub>2</sub> was added through the bottom. The mixture was heated to 70°C as the solvent was evaporated over a 9 hour period. The dry solid was cooled to ambient temperature overnight. Isopentane (5 liters) was added to slurry the solids and the mixture was cooled to 0°C. Ethylene was added to the stirred mixture by a dip tube at a rate of 0.85-1.7 l/min. (0.03-0.06 SCF/min.) until a total of 491 liters of ethylene had been added. Agitation was stopped and the solids allowed to settle. The liquid was decanted from the solids, which were washed twice each with 1.5 liters of isopentane. The wet solids were transferred to a dry-box under N<sub>2</sub> and filtered through a #14 mesh sieve. The fine particles were filtered off, washed with pentane (4 liters) and dried in vacuo. The yield was 326 g.

The polymerization of MCN was conducted in a reactor equipped with a jacket for removing the heat generated by the polymerization reaction. The reactor temperature was set at 55°C. The catalyst (supported rac-dimethylsilanediylbis(2-methyl-4,5-benzo-indenyl)zirconium dichloride activated with methylalumoxane) was fed at a rate

of 18.2 g/hour. The catalyst was fed as a 15% slurry in mineral oil and was flushed into the reactor with propylene. Propylene monomer was fed at a rate of 63.5 kg/hour.

Hexene-1 was delivered at a feed ratio, to the propylene, of 0.05. No hydrogen was added during the polymerization.

Copolymer was produced at a rate of 9.1 kg/hour. The polymer was discharged from the reactor as granular product having a melt flow rate (MFR) of 4.3 and hexene-1 incorporation of 2.8 weight percent. The properties of the metallocene produced copolymer are detailed in Table 1.

The blend of PD9282 E2 and MCN was prepared by the following method. Pellets of the two components, MCN and PD 9282 E2, were dry blended and fed to the hopper of a compounding extruder (Modern Plastics Machinery Corporation, Clifton, N. J.). The extruder was a 2.5 cm (1in.) diameter, 20:1 L/D machine. A melt processing temperature of about 210°C was used. Pellets of the melt homogenized blend were obtained using a strand die. The properties of the blended polymer are detailed in Table 1.

**Table 1**  
**Polymer Properties\***

Polymer	T melt (C)	T crystal (C)	Comonomer (wt%)	MFR dg/min	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Extractables	%Cryst. (Enthalpy)
PD9282 E2	133	90.5	5(C <sub>2</sub> )	5	243,298	2.9	3.3	35.1
MCN	128	93	2.8(C <sub>6</sub> )	4.3	247,825	1.8	0.7	37.3
50:50 MCN/ PD9282 E2	129.5	93.5	2.9(C <sub>2</sub> )	4.6	245,600	2.4	2.1	36.1

\* MFR was determined using the method of ASTM D1238 Condition L. T melt and T crystallization are peak temperatures from Differential Scanning Calorimetry (DSC), run at 10°C/min. heating and cooling rates. Comonomer content was determined via FTIR (Fourier Transform Infrared) measurement (calibrated versus <sup>13</sup>C NMR). Molecular weights and Mw/Mn were determined using Gel Permeation Chromatography (GPC). Percent crystallinity (enthalpy) was derived from the enthalpy of fusion from DSC measurements. 164 J/g is taken from the literature as the enthalpy of fusion of fully crystalline isotactic polypropylene (B. Wunderlich, Macromolecular Physics, Vol. 3, Academic Press, 1980). Extractables testing was determined using n-hexane solvent per the procedure of 21 CFR 177.1520(d)(3)(ii).

The polymers described in Table 1 were used to prepare films as follows. Cast monolayer films were fabricated on a Killion cast coex film line. This line has three 24:1 L/D extruders ('A' extruder at 2.54 cm (1") diameter; 'B' extruder at 1.91 cm (0.75") diameter; and 'C' extruder at 1.91 cm (0.75") diameter) which feed polymer into a fedblock. For monolayer film, the same polymer was fed into all three extruders. The feedblock diverts molten polymer from each extruder to specific channels. The combined streams enter an 20.32 cm (8") wide Cloeren die. Molten polymer exits the die and is cast onto a chill roll (20.3 cm (8") inch diameter, 25.4 cm (10") roll face). The casting unit system is of adjustable speed, to obtain film of the desired thickness. Operating conditions were as shown below in Table 2.

Table 2

Variable	'A' Extruder	'B' Extruder	'C' Extruder
Zone 1 T(C)	218	218	218
Zone 2 T(C)	221	221	221
Zone 3 T(C)	232	232	232
Adapter 1 T(C)	238	238	238
Adapter 2 T(C)	238	238	---
Die/Feedblock (C)	266	---	266
Extr Speed (rpm)	110	96	134
Line Speed (Mpm)	19.8		
Chill Roll T(C)	96		
Gauge ( $\mu$ m)	38.1		

Various properties of the films are shown in Tables 3-7.

**Table 3**  
**Heat Seal Strength (N/15mm) \***

Film/Polymer	Gauge ( $\mu\text{m}$ )	100°C	110°C	115°C	120°C	125°C	130°C
Cast MCN	35.6	0.079	0.21	.56	12.82	12.19	11.04
Cast PD9282 E2	50.8	0.053	0.079	.18	.53	13.53	14.29
Cast Blend	44.7	0.157	1.45	2.77	12.30	13.43	14.35

- 5 \* The films were sealed on a Theller film sealer (Model PC) at the different temperatures shown. After ageing 24 hours, film seal strengths were measured using a United six station machine. The sealing conditions were as follows: 482.65k Pa (70 psi) seal pressure; 1 second dwell time, 12.7 cm (5 inch) x .95 cm (3/8 inch) seal bar dimensions; 2.540 cm (1 inch) wide strips; 3 test specimens per sample; and 50.8 cm (20 inch) per minute test speed. To convert the film thickness to mil, the conversion factor is 1 mil = 25.4  $\mu\text{m}$ .

10

**Table 4**  
**Haze and Gloss**

Film/Polymer	Gauge ( $\mu\text{m}$ )	Total Haze%*	Gloss %*
Cast MCN	35.6	0.6	76.1
Cast PD9282 E2	50.8	5.2	66.7
Cast Blend	44.7	0.3	73.2

\*Haze was measured per ASTM D-1003. Gloss was measured per ASTM D-2457.



**Table 5**  
Dart Impact Strength(g/25.4  $\mu$ m)  
and Elmendorf Tear (g/25.4  $\mu$ m)

Film/Polymer	Dart Impact*	Elmen. Tear-MD*	Elmen. Tear-TD*
Cast MCN	51.4	25.8	53.5
Cast PD9282 E2	59.5	15.4	42.7
Cast Blend	392.6	34.9	149

\*Dart impact strength was measured per ASTM D-1709 and Elmendorf tear strength was measured per ASTM D-1922.

**Table 6**  
Hot Tack Strength (N/15mm)\*

Film/Polymer	Gauge ( $\mu$ m)	100C	110C	115C	120C	125C	130C	140C	150C	160C	170C
Cast MCN	35.6		1.2	1.81	2.03	1.83	1.71	1.2	1.22	0.95	0.74
Cast PD9282 E2	50.8			0.58	1.1	1.43	1.77	1.42	1.23	1.03	0.92
Cast Blend	44.7	0.55	0.86	1.31	1.63	2.08	1.76	1.32	1.22	1.12	0.96

\* Hot tack testing was conducted on a DTC Model 52-D hot tack tester. The testing conditions were: 15mm wide strips; 0.21 N/sqmm seal pressure; 0.5 sec. dwell time, 0.4 sec delay time; and 200 mm/sec peel speed.

**Table 7**  
Film Tensile Strength MPa, Elongation (%), 1%Secant Modulus MPa\*

Film/Polymer	Gauge ( $\mu$ m)	Yield Ten-MD	Yield Ten-TD	Ult Ten-MD	Ult Ten-TD	Ult Elong-MD	Ult Elong-TD	Sec Mod-MD	Sec Mod-TD
Cast MCN	35.6	23.48	24.41	62.74	47.61	535	635	738	765
Cast PD9282 E2	50.8	18.58	18.72	52.19	43.75	635	740	556	562
Cast Blend	44.7	16.55	17.1	58.47	48.19	595	630	467	447

\*Film tensile strength testing was conducted on 2.54 cm (1 inch) wide strips at 50.8 cm/min (20 in/min) (ASTM D 882).

The data of Tables 3-7 show that a blend of the present invention has an attractive balance of properties. The heat seal and hot tack strengths of the blend film are higher than those of the Zeigler-Natta produced polymer film particularly at lower temperatures. The FDA extractables level is likewise better. Surprisingly, the haze of the

blend film is significantly better than that of the Zeigler-Natta produced polymer. Equally surprising is the dart impact strength of the blend film which is substantially better than either of the two individual component films.

5 Also surprising is the fact that the Elmendorf Tear Strength of the blend film is better than either of the two individual component films. The blend film had similar tensile strength and elongation as compared to the component films.

10

The foregoing description is intended to exemplify preferred embodiments of the invention. The invention includes other embodiments not necessarily within the scope of any express example or embodiment recited above. The  
15 invention, therefore, is limited only as set forth in the appended claims.

**CLAIMS**

We claim:

1. A propylene polymer blend composition comprising:

(a) from 25 to 75 weight percent based on the total weight of the polymer blend of a first polymer comprised of at least 80 weight percent propylene units based on the total weight of the polymer wherein the first propylene polymer has a molecular weight distribution of at least 2.5; and

(b) from 25 to 75 weight percent based on the total weight of the polymer blend of a second isotactic propylene polymer comprised of at least 80 weight percent propylene units based on the total weight of the polymer and from 0.2 to 10 weight percent of a second alpha olefin comonomer having 5 or more carbon atoms; wherein the second polymer was prepared using a metallocene catalyst.

2. The composition of claim 1 wherein the first propylene polymer is isotactic.

3. The composition of claim 1 wherein the first and/or the second propylene polymer is substantially isotactic.

4. The composition of any of the preceding claims wherein the first and second propylene polymers are each independently present in the blend in a range of from 40 to 60 weight percent based on the total weight of the blend.

5. The composition of any of the preceding claims wherein the first propylene polymer has a molecular weight distribution in the range of from 3.5 to 7.0.

6. The composition of any of the preceding claims wherein the first propylene polymer is prepared using a Zeigler-Natta catalyst.

5 7. The composition of any of the preceding claims wherein the second propylene polymer is comprised of from 1 to 15 weight percent comonomer.

10 8. The composition of any of the preceding claims wherein the second alpha olefin comonomer is selected from hexene-1 and octene-1.

15 9. The composition of any of the preceding claims wherein the first propylene polymer comprises at least 90 weight percent propylene units and from 2 to 7 weight percent of one or more comonomers.

20 10. The composition of any of the preceding claims wherein the first and second propylene polymers each independently have melt flow rates in the range of from 2 dg/min. to 10 dg/min..

25 11. A propylene polymer blend composition comprising:

(a) from 40 to 60 weight percent based on the total weight of the polymer blend of a first propylene polymer comprised of at least 80 weight percent propylene units based on the total weight of the polymer and from 2 to 7 weight percent of a second alpha olefin comonomer wherein the first propylene polymer is isotactic and has a molecular weight distribution of at least 2.5 and a melt flow rate in the range of from 2 dg/min. to 10 dg/min.; and

35 (b) from 40 to 60 weight percent based on the total weight of the polymer blend of a second isotactic propylene polymer comprised of at least 90 weight percent propylene

units based on the total weight of the polymer and from 1 to 10 weight percent of a second alpha olefin comonomer selected from hexene-1 and octene-1; wherein the second polymer has a melt flow rate in the range of from 2 dg./min. to 10 dg/min. and wherein the second polymer was prepared using a metallocene catalyst.

12. A film at least one layer of which comprises a polymer blend, said blend comprising:

10

(a) from 25 to 75 weight percent based on the total weight of the polymer blend of a first substantially isotactic propylene polymer comprised of at least 80 weight percent propylene units based on the total weight of the polymer wherein the first propylene polymer has a molecular weight distribution of at least 2.5; and

15

(b) from 25 to 75 weight percent based on the total weight of the polymer blend of a second substantially isotactic propylene polymer comprised of at least 80 weight percent propylene units based on the total weight of the polymer and from 0.2 to 10 weight percent of a second alpha olefin comonomer having 5 or more carbon atoms; wherein the second polymer is isotactic and is made using a metallocene catalyst.

20

25

13. The film of claim 12 wherein the first or the second propylene polymer is substantially isotactic.

30

14. The film of claim 12 wherein both the first and the second propylene polymers are isotactic.

35

15. The film of claim 12 wherein the first and second propylene polymers are each independently present in the blend in a range of from 40 to 60 weight percent based on the total weight of the blend.

16. The film of claim 12 wherein the first propylene polymer has a molecular weight distribution in the range of from 3.5 to 7.0.

5 17. The film of claim 12 wherein the first propylene polymer is prepared using a Zeigler-Natta catalyst.

18. The film of claim 12 wherein the second propylene polymer is comprised of from 1 to 15 weight percent  
10 comonomer.

19. The film of claim 12 wherein the second alpha olefin comonomer is selected from hexene-1 and octene-1.

15 20. The film of claim 12 wherein the first propylene polymer comprises at least 90 weight percent propylene units and from 2 to 7 weight percent of one or more comonomers.

20 21. The film of claim 12 wherein the first and second propylene polymers each independently have melt flow rates in the range of from 2 dg/min. to 10 dg/min..

22. A film, at least one layer of which is prepared from  
25 the composition of claim 11.

23. Fabric at least part of which is prepared form the composition of claim 1.

30 24. An article of manufacture at least part of which is prepared from the composition of claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/14847

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L23/14 //(C08L23/14,C08L23:14)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 538 749 (MITSUBISHI PETROCHEMICAL CO) 28 April 1993 see page 2, line 38 - line 57 see page 3, line 43 - page 10, line 45 ---	1-24
P,X	EP,A,0 716 121 (MITSUI PETROCHEMICAL IND) 12 June 1996 see page 3, line 26 - line 38 see page 5, line 10 - page 23, line 25 ---	1,2
X	EP,A,0 646 624 (MITSUI PETROCHEMICAL IND) 5 April 1995 see page 4, line 57 - page 5, line 21 -----	1-24



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/14847

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		DE-T- 69201180	14-06-95
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		CA-A- 2164461	07-06-96
		JP-A- 8208909	13-08-96
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